Reduction of micro-object's adhesion using chemical functionalisation

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Abstract

The adhesion and interaction properties of functionalised surfaces (substrate or cantilever) were investigated by means of atomic force microscope (AFM) related force measurements. The surfaces were functionalised with a polyelectrolyte: Poly(Allylamine Hydrochloride) (PAH), or with silanes: 3 (ethoxydimethylsilyl) propyl amine (APTES) or (3 aminopropyl) triethoxysilane (APDMES). Measurements of forces acting between a bare glass sphere (functionalised or not) and a functionalised surface indicated repulsive or attractive forces, depending on functionnalisation and medium (wet or dry). Adhesion forces (pull-off) can be observed in dry medium while in wet medium, this phenomenon can be cancelled. Now, the pull-off forces is an important problem in the automation of micro-object manipulations. The cancellation of this force by chemical functionnalisation is thus a promising way to improve micro-assembly in the future.

Introduction

Manufactured products are becoming always smaller and are integrating more and more functionalities in small volumes. Several application fields are concerned by the Micro-Electro-Mechanical-Systems (MEMS) such as the telephony, bio-engineering, telecommunications. The assembly of these microproducts is a great challenge because of the microscopic sizes of the components. In fact, the major difficulties of micro-assembly come from the particularity of the micro-object's behaviours which depend on surface forces [1, 2, 3]. The manipulation of a micro-object requires

to handle, position, and release it without disturbances of the surface forces such as electrostatic forces, van der Waals forces or capillary forces. The release is the more critical phase which is usually hindered by adhesion.

Several methods have been proposed in the last ten years to improve micromanipulations [4, 5]. The first approach consists in using non-contact manipulations like laser trapping [6] or dielectrophoresis [7]. These manipulation methods are not disturbed by adhesion but the blocking force stays low which is a major drawback when applied in microassembly. The second approach deals with contact manipulation where the adhesion is reduced or directly used for manipulation. The reduction of the adhesion can be achieved for example by adding roughness on the end-effectors [8, 9]. Adhesion can be directly used to perform manipulations. In this case, one-fingered gripper is sufficient to handle objects, but the release stays difficult [10]. The release requires in fact new methods such as the inertial release [11] or dielectrophoresis release [12]. In contact handling, the blocking force is usually high. The current microhandling methods are able to improve micromanipulations but the object's behaviour is always disturbed by adhesion and the reliability is still low [9, 13].

We propose a new way in contact handling which consists in chemically controlling the surface forces between the object and the gripper. The major objective is to reduce the adhesion force or to create a repulsive force to guarantee a reliable release. This paper shows that the tested functionnalisations are able to significantly reduce adhesion. As adhesion is the major disturbance in micro-handling, this fact directly shows the potentiality of using functionalised microgripper to assemble microparts. This paper based on interaction force measurements consequently shows the potentiality of this approach.

Now, the surface properties of a material can be controlled by surface functionnalisation. The surface functionnalisation of the objects or of the grippers can be obtained by different methods. The two more important methods are the physisorption of polyelectrolyte (polyelectrolyte with positive or negative charges) [14] or the grafting of molecules on the surface (covalent bound between the substrate and the molecules) [15, 16, 17] in order to form a self-assemble monolayers.This phenomenon is mainly due to two processes depending of the instrinsic atomic compositions of the substrates: Oxydized substrates are useful for silane functionalisation whereas gold substrates are only reactive with sulfhydrils compounds. The difference in reactivity could be a real advantage in our approach because the using of silane (or thiol) molecules will allow a vectorization of the chemical processes. This could be a highly versatile tool box to give specific properties to a precise part of the micro-objects especially in the real world of micro-assembling.

The first method induces electrostatic interaction between the substrate and the polyelectrolyte. There is no bounding between the substrate and the adsorbed molecules. The electrostatic interaction can be modified during the adsorption or after by the pH and the ionic strength of the bulk, and by the humidity in dry medium. The polyelec-

trolyte used can be strong (totally ionised whatever the pH or the ionic strength) or weak (ionisation changed with the pH or the ionic strength). The polyelectrolytes adsorption takes place in aqueous solution. So two substrates can be functionalised with complementary charges (positive for one and negative for the other one) or identical charges in order to generate electrostatic interaction respectively attractive or repulsive forces. Usually, several polyelectrolyte layers are necessary in order to increase the attractions of the microstructures. The second method generates covalent bound between substrate and molecules. These molecules must contain silanol, thiol, azide, allyl or vinyl groups [15, 16] in an extremity. These molecules have to be used in organic solvent as toluene, acetone, methanol, ethanol, ... The silanol create a bound Si-O-Si with the silica substrate [15] while allyl or vinyl generates Si-O-C (or Si-C) bound [18] and the azide groups produce Si-N bound [19].

Consequently, we are proposing to improve micromanipulations by using functionalised objects and gripper to control contact interaction. This article focuses on the feasibility of this approach based on the measurement of attractive and repulsive force in function of the medium. The chemical surface functionnalization is presented in the following section. Experiments and control of the interactive force using the medium are showed in the section 3.

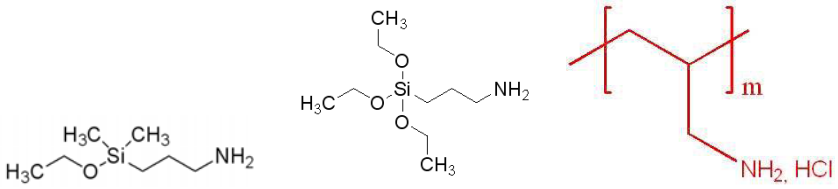
1 Experimental procedures

1.1 Materials and chemicals

The polyelectrolyte, Poly(Allylamine Hydrochloride) (PAH), with an average molecular weight of 70 kDa and the silanes: 3 (ethoxydimethylsilyl) propyl amine (APTES) and (3 aminopropyl) triethoxysilane (APDMES), figure 1, ethanol and sodium chloride (NaCl),were purchased from Sigma Aldrich. The three chemical compounds (PAH, APTES, APDMES) used to surface functionnality are an amine function NH_2 which can protonated or ionised to NH_3^+ according to pH. In acidic pH, the anime is totally ionised, then the ionisation decreases and is null in basic pH (between pH 9 and 12). The deposits were made on SiFiT (silicon Fingers Tips) design in the Department. The Milli Q water was obtained with the Direct-Q 3 of Millipore.

1.2 Surface functionalisations

Before being functionalised, the wafers were cleaned by immersion in a piranha solution (2 parts H_2SO_4, 1 part H_2O_2) during 25 minutes at 70°C. Then, the wafers were rinsed, stored in Milli Q water before PAH functionalisation or rinsed in milli Q water and in ethanol before silanisation (functionalisation by silane: APDMES, APTES). Solutions were freshly prepared by direct dissolution in milli-Q quality water and in ethanol for respectively the PAH and the



(a) APDMES (b) APTES (c) PAH

Figure 1: Molecules used for the silica functionnalisations.

silanes. The final silanes concentration was of 1% . The PAH solution was a polymer concentration of 10 mg/ml, and ionic strength of 0.5 M in NaCl, and a pH of 9. The surfaces were functionalised by immersion in solutions during one night at room temperature. In the polymer solution, the PAH was just adsorbed in the surface (no covalent bound) and in the silanes solution, the silanes were gratfed on the substrate (covalent bound). The excess of ungrafted silanes was removed by ultrasonication during 2 mins in ethanol.

1.3 functionalisation mechanisms

1.3.1 PAH adsorption

The protonation of the PAH is partial at pH 9 (near 40 %) [20, 21]. In the bulk the NH_2 functions of the PAH were ionised to NH_3^+ . When the substrate (silica last layer), negatively charged from pH 5 [22], is immersed in the cationic PAH solution, the cationic polymer chains are electrostatically attracted by the negative charges covering the substrate. Thus, silica layer counter-ions, are substituted by cationic polymer chains, transported by diffusion near the substrate, and a surface ion pairing occurs between polymer chains and silica negative charges. Consequently, the mechanism of deposition is based on the substitution of the silica counter-ions by charged polyelectrolyte. This fixation is possible thanks to the electrostatic affinity between the cationic PAH and the negatively charged substrate. It is the physisorption reaction with no covalent bound.

1.3.2 Grafted silanes

The mechanism of self-assembled monolayers formation during silanization process is depicted in figure 2, which takes place in four steps [23, 24]. The first step is physisorption, in which the silane molecules get physisorbed at the hydrated silicon surface. In the second step, the silane head-groups arriving close to the substrate hydrolyse in the presence of the adsorbed water layer on the surface ,into highly polar trihydroxysilane $Si(OH)_3$ or hydroxysilane

$Si(OH)(Me)_2$ for respectively triethoxysilane $Si(OEt)_3$ (APTES) and ethoxysilane Si(OEt) (APDMES). These polars groups ($Si(OH)_3$ or Si(OH)) form covalent bonds with the hydroxyl groups on SiO_2 surface (third step) subsequently to which condensation reaction (release of water molecules) goes on between silanol functions of neighbour molecules. Self-assembly is driven by lipophilic interactions between the linear alkane. During initial period, only a few molecules will adsorb (by steps 1-3) on the surface and the monolayer will definitely be in a disordered (or liquid) state. However, at longer times, the surface coverage eventually reaches the point where a well-ordered and compact (or crystalline) monolayer is obtained (step 4), for APTES only, by the condensation reaction between the APTES molecules.

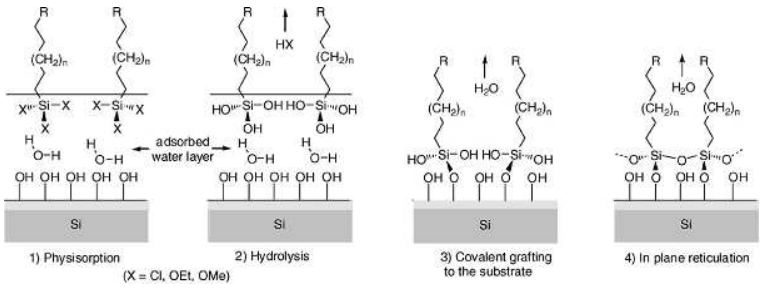


Figure 2: Steps involved in the mechanism of SAM formation on a hydrated silicon surface [23, 24].

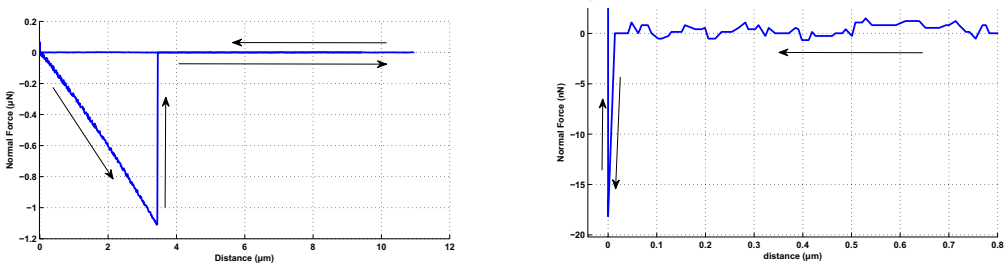
1.4 Force-Distance Measurement

Force-distance measurement were performed using a stand-alone SMENA scanning probe microscope (NT-MDT) in order to characterize the functionalisation. The AFM has an optical deflection measure with a laser diode, a beam and a Sensitive PhotoDiode. The SPD is a sensor with 4 quadrants shapes giving 2 values for one deflection (normal (flexion) and one lateral (torsion) signal). The AFM cantilever, whose stiffness is 0.3N/m, was fixed and the sample moved vertically. Each measurement was performed with a silicon rectangular cantilever (Novascan Technologies, Ames, USA) where a borosilicate sphere (borosilicate, 10 μm diameter) was glued onto the apex of the tipless (Ref.:*PT.BORO.SI.10*, company Novascan Technologies, Ames, USA). As applicative objective of this work is to improve reliability of micro-object manipulation, interactions have been studied between a *micrometric* sphere (10 μm diameter) and a plane. All measurements were done at the driving speed of 200 nm/s to avoid the influence of the hydrodynamic drag forces [25, 26] in liquid medium. Experiments in air were done with humidity percent near 30%. For each sample, nine measures were done in different points. The repeatability of all the measure of pull-off and pull-in forces was better than 10 %.

2 Experimental results

2.1 functionalised surface

We started with the study of the interaction and adhesion properties in dry and wet media. The force distance curves were measured just after functionalisation of the surface with a non fonctionnalised cantilever. The surface functionalisation modifies the interaction between the surface and the cantilever. Indeed, before functionalisation, there is a less repulsion between the two surfaces because of the negative charge on the surface due to the silanol groups, and after surface functionalisation, we measured attractive forces (near -20 nN, figure 3.b) for all the chemical functionalisation used. An example is presented in Figure 3 for the APTES gratfed silane on silica. The point 0 on the distance axis corresponds to the contact point between the cantilever and the surface.



(a) Total curve (b) near the contact point

Figure 3: Force-distance curves on the substrate functionalised APTES in dry medium obtained with a tip which spring constant is 0.3 N/m.

In Figure 3, ~~there is no hysteresis between forces measured on approach and on retract.~~ we clearly measured a pull-off force which represents the adhesion between the glass sphere on the tip and the functionalised substrate. For example in Figure 3.a , the pull-off force is reading 1.1 μN. The same experiments were done with the other chemical compounds (adsorpted or grafted molecules on the substrate) in wet and dry media. The average of the nine different measures realized on three places, adhesion and approach forces, for the two mediums, are summarized in the table 1.

The pull-in and pull-off forces change with the functionalisation and the medium. Indeed, in dry medium, the pull-in forces are low (about ten nano Newtons) perhaps because the charge is compensated by counter ions and their mobility is very low. The adhesion, in dry medium, of the surface functionalised with APTES is more important than PAH and APDMES. This difference can be explained by the fact that the layer of APTES reaches the point

	Dry medium		Wet medium	
functionalisation	Pull-in (nN)	Pull-off (nN)	Pull-in (nN)	Pull-off (nN)
APDMES	-4.97 ± 1	-769 ± 72	-29.8 ± 6	-353 ± 21
APTES	-13.2 ± 1.5	-1150 ± 90	-59.5 ± 8	-387 ± 38
PAH	-11.7 ± 1.1	-720 ± 67	-24.3 ± 6	-310 ± 27

Table 1: Influence of the surface functionalisation in dry and wet medium on the Pull-in (nN) and Pull-off (adhesion forces)(μN) obtained with a tip whose spring constant is 0.3 N/m.

where a well-ordered and compact (or crystalline) monolayer is obtained (step 4, Figure 2), and by the fact that during the surface functionalisation, the silanisation reaction can be done between one silane grafted with the surface and free silane not grafted in solution.

In wet medium, the pull-in forces increased but they didn't arrive at very important values because the pH of the Milli Q water is near pH 5.5 and at this pH, the silica charges are not very important. The pull-off forces decrease compared to dry medium, because of the increase of the mobility of the counter ions. Indeed, the counter ions can more rapidly compensate the cantilever and the surface charges during the surface retract.

To conclude on this part, the micro-assembly of structures could be done in wet medium which decreases their adhesion. In order to manipulate and to assemble micro-objects, we are going to show that the adhesion can also be completely cancelled by functionalisation of both substrate and sphere on AFM cantilever.

2.2 functionalised surface and cantilever

The cantilever functionalisation was only done with the APTES silane and with no sonification step. The force-distance curves were realized in the same conditions as previously, dry and wet medium, three surfaces functionalised (APTES, APDMES, PAH). In this case, there are no attraction but repulsion between all the functionalised surface and functionalised cantilever. The Figure 4 presents the example of the PAH surface in wet medium.

We observe a repulsion (positive pull-in force near 0.8 μN) and no pull-off force between the two funtionnalised surfaces, and a slight hysteresis between forces measured on approach and retract. The average values of the nine different measures realized on three places, (pull-in and pull-off forces), for the two mediums, are summarized in the table 2.

In this table 2, the pull-in forces are null in dry medium and appear clearly repulsive in wet medium. There are not important differences between the three chemical compounds on pull-in force in liquid medium. The cantilever and the surface have the same positive charges due to the anime functions which are practically completely ionised in MilliQ water (pH 5.5), so in the form NH_3^+. However, the pull-off forces with PAH adsorded on the subtraste

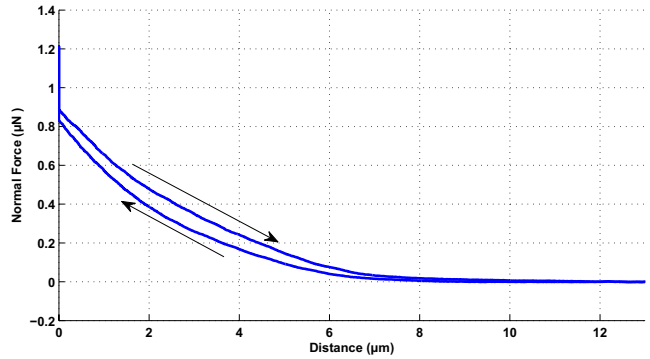


Figure 4: Force-distance curve for the PAH functionalised substrate in wet medium obtained with a tip whose spring constant is 0.3 N/m.

	Dry medium		Wet medium	
functionalisation	Pull-in (nN)	Pull-off (nN)	Pull-in (μN)	Pull-off (nN)
APDMES	0	-136 $\pm$ 35	735 $\pm$ 60	0
APTES	0	-91 $\pm$ 23	655 $\pm$ 50	0
PAH	0	-801 $\pm$ 58	774 $\pm$ 67	0

Table 2: Influence of the surface functionalisation on APTES grafted on cantilever in dry and wet medium on the Pull-in (nN), Pull-off (μN) obtained with a tip which spring constant is 0.3 N/m.

is more important than the surface with silane grafted and it is near the same value with no functionnality on the cantilever (table 1). We can explain this, by the fact that PAH is just adsorbed on the surface and not grafted. So when the cantilever is in contact with the surface, the PAH molecules adsorbed on the cantilever and on the surface move in order to create the better interaction between surface and cantilever as in the case surface was functionalised and cantilever free of molecules.

The cancellation of the pull-off force in wet medium is a great opportunity in the application field of micromanipulation. In fact, the handling of functionalised micro-objects with functionalised grippers in a liquid could be done without adhesion disturbances. Future works will focus on the application of this first result on experimental micromanipulations in order to definitively show the relevance of functionalized grippers in robotic microhandling.

Conclusion

In this paper, we have studied adhesion behaviours between functionalised surfaces and functionalised or neutral micrometric sphere. The experiments were done in wet and dry medium. The surface are functionalised by three

chemical compounds using two different ways of functionalisation: adsorption of polyelectrolytes (PAH) and silanisation (grafted of silane molecules). We have shown that the functionalisation and the medium could highly change the adhesion properties. The micro-assembly could be facilitated by a judicious choice of the media and of the functionalisation of grippers and micro-objects. If the object is not functionalised, the manipulation in a wet media can, in fact, reduce the pull-off forces. Pertubations will be thus reduced in wet medium. Moreover, if the object is functionalised, the wet medium can be used to simply cancel the adhesion. As adhesion is the current highest pertubation phenomenon in micromanipulation, functionalisation is a promising way to improve micro-object manipulation in the future.

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